

ON THE ELECTROCATALYSIS OF OXIDATION OF SMALL ORGANIC MOLECULES. HIGHLIGHTS OF THE LAST FIVE YEARS

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In the last years a lot of effort has been devoted to the study of electrochemical processes involving small organic molecules (methanol, formic acid, reduced CO₂ and ethanol among others). These efforts have thrown new basic knowledge on the electrocatalysis of the processes involving these species.

Influence of adsorbed water

One of the most important steps was the knowledge gained on the role of adsorbed water in oxidation processes of small organic molecules. The anodic peaks during the negative-going sweep of a voltammogram at Pt is due to the competitive adsorption of water and organics in the so-called double layer region of the voltammogram [1].

Methanol

At PtRu all reaction steps of methanol oxidation, namely adsorption, oxidation of adsorbed residues and the parallel process involving HCOOH formation are favored. In the voltammogram of Fig. 1 it can be observed that the first sweep for a Pt electrode exhibits two maxima, the first of them, at ca 240 mV, corresponds to adsorption and dissociation of methanol and the second one at about 430 mV is related to the parallel pathway producing HCOOH. The latter reacts with excess methanol to form methyl formate (m/e = 60, lower part). At PtRu both these processes are shifted to negative potentials.

PtRu binary catalysts prepared by different procedures (alloys, adsorbed Ru onto Pt, deposited Pt and Ru onto an inert substrate) have catalytic effects on methanol oxidation. All of them have a maximum activity for Pt:Ru ratios between 15 and 45%, alloys being the best materials [2].

Disordered (rough) Pt surfaces do not exhibit the typical decay of current at constant potential, a characteristic of smooth electrodes. The decay originates in two processes: formation of (inactive) Ru-oxides and poisoning with organic residues [3].

Reduced CO₂

Formation of formic acid and methanol during CO₂ reduction by adsorbed hydrogen at polycrystalline Pt in acid medium has been shown by in situ FTIR and on-line MS spectra.

Ethanol

The ratio CO₂/acetic acid is much higher at porous than at smooth PtRu electrodes as demonstrated via in situ FTIR (Fig. 2). The latter material shows a higher ability to breaking the C-C bond.

Carbon monoxide

For the oxidation of bulk CO, *pure ruthenium* is a better catalyst than (50:50)PtRu. The latter exhibits the best performance for stripping of adsorbed CO.

FTIR spectra shows that on Ru electrodes the band center for the CO stretching shifts strongly towards higher frequencies from 0.3V upwards indicating a weakening of the Metal-CO bond as the formation of adsorbed OH on Ru begins.

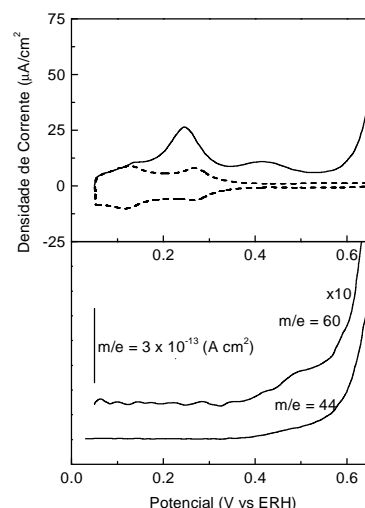


Fig. 1 On line MS experiment during oxidation of 1.0 M CH₃OH + 0.5 M H₂SO₄ on polycrystalline Pt.

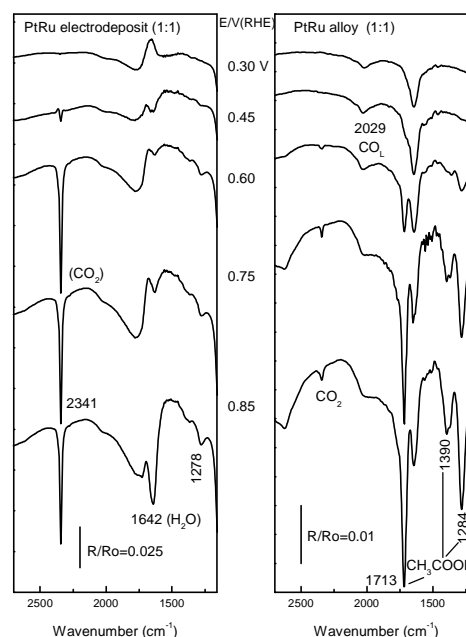


Fig. 2. FTIRs for ethanol oxidation at PtRu (1:1) in 0.1M EtOH + 0.1M HClO₄. Ref. spectrum: 50 mV

References

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Acknowledgments

Financial support from DFG and Fonds der Chemischen Industrie (Germany) and from FAPESP (Brazil) is gratefully acknowledged.